Pacific Science (1974), Vol. 28, No. 3, p. 225–245
Printed in Great Britain

Processes of Carbon Dioxide Flux in the Fanning Island Lagoon[1]

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ABSTRACT: Carbon dioxide follows a variety of transfer pathways through marine systems, and a budget of CO_2 can be used to enumerate those pathways. In a coral reef system, the biogeochemical pathways of organic carbon production-consumption and calcification are likely to be prominent. We measured the temperature, salinity, *p*H, and total alkalinity of about 400 water samples to describe the CO_2 budget of the lagoon at Fanning Island, Line Islands, during July and August 1972.

Mean lagoon salinity was about 31.5‰, or 3.3‰ below the open ocean salinity there, as a result of heavy rainfall and groundwater seepage. This salinity depression, together with data on rainfall and tides, was used to calculate a mean lagoon water residence time of about 1 month.

The CO_2 budget of the lagoon water can be described in terms of processes altering the ocean water composition. Gas exchange accounted for a net CO_2 evasion of less than 1.4 moles m^{-2} $month^{-1}$. Freshwater dilution lowered the CO_2 content by about 0.5 moles m^{-2} $month^{-1}$. Calcification lowered CO_2 by 0.9 moles m^{-2} $month^{-1}$; and CO_2 changes attributable to organic carbon transfer lay between -0.1 and $+1.3$ moles m^{-2} $month^{-1}$.

Net organic carbon transfer in the lagoon is near zero, suggesting a close balance between organic carbon production and consumption. Calcification is about 1 kg $CaCO_3$ m^{-2} yr^{-1}, much lower than the rate which can be estimated from the standing crop and expected growth rate of corals there. It seems possible that the CO_2 system of Fanning Lagoon, and perhaps that of other coral reefs as well, may be potentially limiting to biological activity.

Carbon dioxide is involved in a variety of processes affecting coral atolls. The high rate of gross organic carbon productivity and skeletal calcium carbonate precipitation attest to the biogeochemical importance of CO_2 in such a system. Physical processes such as evaporation, rainfall, and freshwater seepage also can alter the CO_2 content of atoll water. All of these processes change the CO_2 concentration, and thereby alter the CO_2 partial pressure from that of the neighboring oceanic waters. Such alterations affect the transfer rate of CO_2 across the air-sea interface.

The present investigation was designed to describe the CO_2 budget for the lagoon of a coral atoll. Thus, CO_2 serves as a tracer which clarifies the behavior of processes within the lagoon system. Moreover, some of the interdependencies which emerge suggest possible mechanisms which merit more detailed future investigation.

Fanning Island (4° N, 159° W, in the Line Islands) is the site of the present investigation. Unlike most atoll lagoons, Fanning Lagoon is almost entirely surrounded by islands rather than by reefs. Despite being nearly landlocked, the lagoon supports abundant and diverse reef biota, apparently similar to that of less restricted lagoons. Therefore, the physiographic peculiarities which make the lagoon convenient to study do not detract from the likelihood that we

[1] Hawaii Institute of Geophysics contribution no. 603. Hawaii Institute of Marine Biology contribution no. 432. Coral Reef Management and Research contribution no. 8. The research was supported by National Science Foundation grant no. F331-0-260-3230. Manuscript received 1 September 1973.

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can use our results to draw conclusions about atoll lagoons in general.

Experimental Design and the CO_2 System

The CO_2 content of lagoon water results from a variety of processes. Each process imparts distinctive characteristics upon the lagoon water, so we can at least partially isolate the various processes. Both the concentration and the state of CO_2 in the water, along with the salinity of that water, are used in calculating this budget.

Mixing several water types results in water with an intermediate composition. Three water masses enter into such mixtures at Fanning: ocean water, rainwater, and groundwater.

Internal chemical reactions alter both the total CO_2 content and the partitioning of CO_2 species in the water. The primary internal reactions affecting CO_2 in seawater are $CaCO_3$ precipitation-solution (here termed "net calcification") and organic carbon production-respiration ("net production"). Both processes lower the total CO_2 content of seawater by 1 mole for each mole of carbon produced. Calcification lowers the total alkalinity of seawater by two equivalents for each mole of $CaCO_3$ precipitated, while net organic carbon production does not alter the total alkalinity (see Park 1969, Smith 1973).

The partial pressure of CO_2 in seawater is sensitive to any process which alters the amount and partitioning of dissolved CO_2 constituents in the water. Moreover, net CO_2 flux across the air-sea interface is driven by any differential CO_2 partial pressure across that interface (Kanwisher 1963; Sugiura, Ibert, and Hood 1963). Hence, the preceeding processes alter the CO_2 exchange rate in the lagoon from that of the adjacent open ocean.

The Fanning Lagoon is a partially isolated body of water which exchanges its water with oceanic water through the flushing action of tidal currents which reverse their flow semi-diurnally. The CO_2 alteration processes mentioned above act to prevent the lagoon water from reaching the composition of the ocean-water source. Let us consider the lagoon to be a well-mixed, constant-volume system, continually flushed by water from an infinite reservoir of constant composition. A random sample of this lagoon water will have a composition reflecting the rate at which the processes within the lagoon act relative to rate of replenishment with ocean water (residence time). It is convenient to express the relationship among the rate of internal alterations (A) by some process, the composition difference between the ocean and lagoon (ΔX), and the lagoon water residence time (τ) by means of a simple equation:

$$A = \Delta X/\tau \qquad (1)$$

A is in the units' rate of change per unit volume of lagoon water. Multiplying A by the mean water depth of the lagoon will yield the units' rate of change per unit area of lagoon floor. The above model assumes a time-series steady state and spatial homogeneity. We will discuss and defend the steady-state assumption; substituting average values from a lagoonwide array of data for one random sample overcomes the obvious inhomogeneity of lagoon waters.

METHODS

Field Techniques

Over 400 water samples were collected from more than 100 localities at Fanning Island. Samples were collected at the localities shown in Fig. 1. Surface water was scooped directly into 1-gallon plastic bottles. Samples 2 meters below the surface and within 1 meter of the lagoon bottom were pumped into the bottles with the immersion pump described by Schiesser (1970). Water temperature was measured by placing a thermometer in the sample bottles as the samples were collected.

Except for specific tide-cycle, or diurnal-cycle sampling, most samples were collected before midday to minimize the effect of any diurnal cyclicity which might bias wide-area sampling. Samples sat on the open deck of our skiff (but were usually within about 2° C of their 29° C average collection temperature) from a few minutes up to a maximum of about 5 hours before they were returned to the laboratory for analysis. Most samples were returned to the lab within 2 hours of their collection time. Up to 15 sample stations were occupied during a single day.

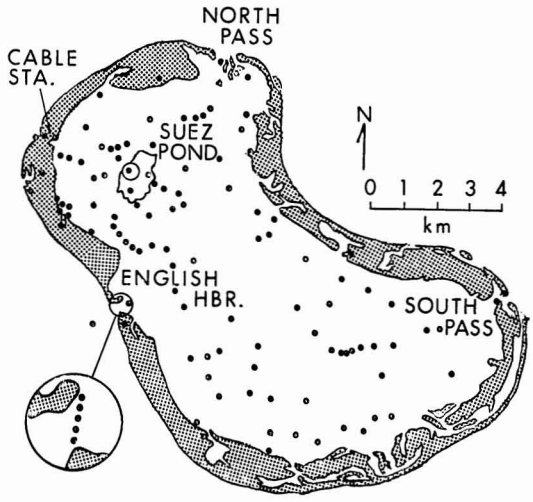

FIG. 1. Index map of Fanning Island station locations. Locations discussed by name are shown on the map, and the sites of the Suez Pond 1-day survey and the English Harbor tide-cycle survey are circled.

Besides the wide-area sampling, three levels of time-series samples are reported here. Water was collected near noon each day for about 10 days at Suez Pond. Suez Pond was also sampled approximately every 2 hours over one 26-hour period. Repeated sampling at five locations across the mouth of English Harbor was done over one 13-hour period. These named sample localities are identified on Fig. 1.

Laboratory Analysis

Our laboratory at the cable station (Fig. 1) was an air-conditioned room maintained near 25° C. Samples were returned to that room as quickly as possible after collection, left for an hour or more to approach room temperature, and then analyzed.

Salinity was measured with a Bissett-Berman model no. 6230 conductivity salinometer. Alkalinity and *p*H were measured with an Orion model no. 801 *p*H meter and Beckman electrodes (no. 1617 *p*H; no. 1615 reference).

We soaked the electrodes in slightly acidified tap water overnight between analysis periods and calibrated the meter with commercial buffers (*p*H 7.00 and 4.01) before the day's analyses. We next soaked the electrodes for at least 1 hour in acidified seawater and then ran an initial dummy alkalinity measurement to stabilize the electrodes before we analyzed a batch of alkalinity samples; we did not rinse the electrodes between analyses. We then soaked the electrodes in unacidified seawater until *p*H readings stabilized before we measured a batch of seawater *p*H values. *p*H measurements were made on unfiltered water samples.

Alkalinity measurements were made according to the procedure of Culberson, Pytkowicz, and Hawley (1970) with water filtered with a Millipore 0.8-μ pore-size filter, plastic in-line filter holder, and plastic syringe. Titrisol, commercially available prestandardized HCl, was diluted to 0.010 N and used for the analyses. Analytical precision was not a limiting consideration, so only single analyses were run on most samples.

As outlined in the appendix, calculations of the various parameters in the CO_2 system follow from the temperature, salinity, *p*H, and total alkalinity data.

RESULTS

Water Composition at Fanning Island

The waters of Fanning Island can be divided into four categories, each with its distinctive composition: oceanic water, lagoon water, groundwater, and rainwater. Table 1 summarizes mean salinity and CO_2 characteristics for these water types.

About 20 samples of inflowing water at English Harbor provided the primary record of ocean water composition. This material had a constant composition. Salinity (S) was 34.8‰; total alkalinity ($T.A.$) was 2.35 meq/liter; and *p*H was 8.25. These values yield a total CO_2 content (ΣCO_2) of 2.0 mmoles/liter and a specific alkalinity ($S.A. = T.A./Cl$) of 0.122.

Lagoon water varied widely in composition, as is evident from maps of salinity (Fig. 2); but a large amount of data was available for calculating mean composition of the lagoon. Planimetry of the area between contour lines on maps of salinity, specific alkalinity, and *p*H yields mean lagoon values of 31.5, 0.108, and 8.1‰, respectively. From these values, a mean total alkalinity of 1.9 meq/liter and a mean total CO_2 content of 1.7 mmoles/liter can be calculated.

A limited number of samples (10) and the

TABLE 1

COMPOSITION OF MAJOR WATER MASSES AT FANNING ISLAND

WATER MASS	SALINITY (‰)	*p*H	TOTAL ALKALINITY (meq/liter)	ΣCO_2 (mmoles/liter)	SPECIFIC ALKALINITY (*T.A.*/chlorinity)
Open Ocean	34.8	8.25	2.35	2.0	0.122
Lagoon	31.5	8.1	1.9	1.7	0.108
Rainwater	0.0	6.4	0.0	0.0	–
Groundwater	0.0	7.7	3–5*	3–5*	–

* These are subjective estimates based on the most frequent values encountered rather than being mean values.

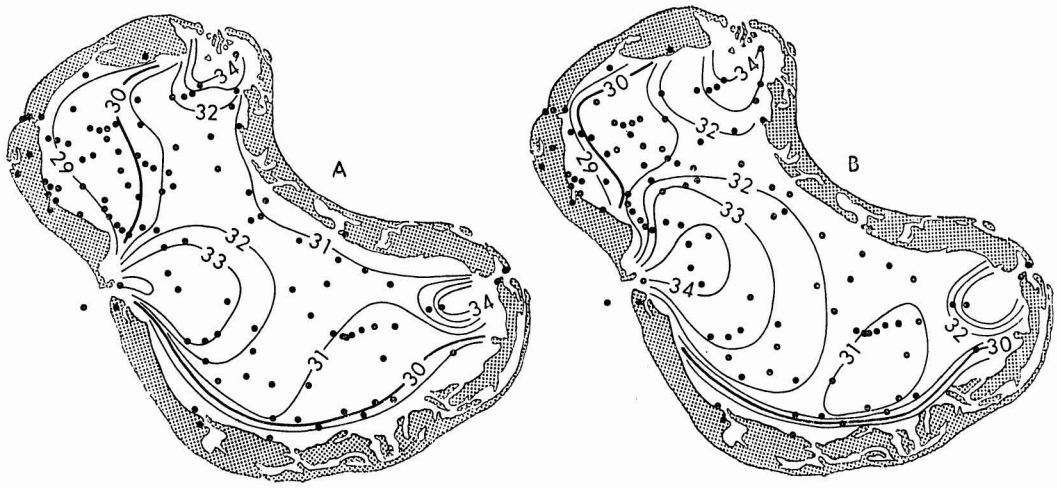

FIG. 2. Maps of surface (A) and near-bottom (B) lagoon salinity at Fanning Island.

extreme variability of these samples made groundwater composition difficult to characterize. All samples had a salinity near 0‰, and a *p*H between 7.6 and 7.9. Total alkalinity ranged from 1.5 to 6.8 meq/liter. It will become evident that our interpretation of the effects of various processes on CO_2 composition of Fanning waters is not particularly sensitive to our estimate of the exact groundwater composition. We initially judge "typical" groundwater total alkalinity to have been about 3 meq/liter, but we then consider in our calculations the possibility that a typical groundwater alkalinity value might have been as high as 5 meq/liter. To a first approximation, the total CO_2 content of the groundwater equals alkalinity at the *p*H of these waters.

Rainwater was a significant water type during our stay. If rainwater *p*H (measured to be about 6.4) is considered to result from the solution of CO_2 in distilled water, then rainwater contained about 10^{-3} mmoles/liter total CO_2. Rainwater salinity was not measurably different from 0‰.

Fanning Lagoon Water Budget

Some volume of ocean water (V_O) enters the lagoon each day. Rainwater (V_R) is a second major source of water entering the lagoon. Some of the ocean water and rainwater entering the lagoon each day stays there, and some is exchanged for lagoon water which departs (V_E). If the lagoon volume is to remain constant (after adjustment has been made for tidal variations), then V_E must equal the sum of V_O plus V_R; or, by rearrangement:

$$V_O = V_E - V_R \qquad (2)$$

Actually, two other terms also enter into this equation, but they are small and approximately offset one another. Data given by Wyrtki (1966) demonstrate that evaporation in the vicinity of Fanning Island ordinarily amounts to about 0.3 cm/day during the months of July and August. That value is about 20 percent of the 1.5 cm/day mean rainfall which was measured at two rain gauges during those months in 1972; the weather conditions associated with the high rainfall during that period probably lowered evaporation well below this usual rate.

Groundwater seepage adds water to the lagoon. Zipser and Taylor (1968) list the land area of the atoll to be one-fifth as large as the lagoon area. Data by Guinther (this issue) suggest that the freshwater lens of Fanning was filled to capacity during the summer of 1972 and that rainwater falling on the islands quickly seeped into the ocean and lagoon. If half this seepage entered the lagoon, and if lagoon and island rainfall per unit area equaled one another, then groundwater provided about one-tenth as much water to the lagoon as did direct rainfall.

Combined evaporation and groundwater apparently lower the total fresh water contribution to the lagoon less than 10 percent below the rainfall contribution; therefore, equation (2) is an adequate representation of the water budget.

Residence Time Water in Fanning Lagoon

Gallagher et al. (1971) presented an approach to estimating one extreme limit of water residence time in the lagoon, and a second extreme can be extracted from their discussion. Residence time (τ, in days) is the water volume of the lagoon (V_L) divided by the daily net volume of lagoon water exchanged for ocean water and rainwater (V_E, equation 2):

$$\tau = V_L/V_E \qquad (3)$$

Exchange of ocean and lagoon water occurs almost entirely at the three passes between the ocean and the lagoon and is accomplished almost entirely by tidal flow. Gallagher et al. (1971) found that, over a 24-hour period, about 95 percent of the total water inflow and outflow occurred at English Harbor. That pass had a slight net outflow of water on a tide cycle, while both of the smaller passes had a net inflow.

By assuming the only net exchange over 24 hours to be accomplished through the excess of water inflow over outflow at the two eastern passes, Gallagher et al. (1971) arrived at a "lower" (longer) limit of lagoon water residence time. They took the lagoon volume to be 4.1×10^8 m^3 and the net input at the two eastern passes to be 1.2×10^6 m^3 day^{-1}. These values yield a residence time estimate of 340 days, according to equation (3).

An "upper" (shorter) limit on residence time can also be derived from the study by Gallagher et al. (1971). Those authors point out that the semidiurnal tidal exchange is equivalent to about 5 percent of the lagoon volume. If all incoming ocean water were to displace lagoon water without mixing, then 20 periods of inflow (about 10 days) would be needed to replace all the lagoon water. The correct residence time cannot be shorter than this value.

The best estimate of residence time obviously lies somewhere between these broad extremes. An ocean-to-lagoon salinity differential set up by the heavy rainfall preceding and during our 1972 expedition provided a basis for getting at this best estimate. Two different approaches presented here yield comparable results. Water was sampled eight times at each of four localities across the English Harbor Pass during a tide cycle. Incoming water had a near-constant salinity of 34.8‰ (Table 1). Outgoing water was more variable in composition but averaged 33.8‰. The mean lagoon salinity was approximately 31.5‰ (Table 1). If χ is the proportion of lagoon water exiting English Harbor, then:

$$31.5\,(\chi) + 34.8\,(1-\chi) = 33.8$$
$$\text{and} \qquad \chi = 0.30 \qquad (4)$$

As discussed above, about 10 percent of the lagoon volume takes part in daily tidal exchange. If 30 percent of the total daily outflow through the passes on ebb tides is lagoon water, then according to this calculation 3 percent of the lagoon water is removed daily, and the mean residence time is 33 days.

A second method of estimating lagoon residence time from the salinity differential makes use of available rainfall data. Because high and relatively constant rainfall had

occurred for well over a month preceding our lagoon salinity survey, it was assumed that lagoon salinity had reached a steady state value. Rain gauges at the cable station and at English Harbor showed considerable day-to-day differences from one to the other but recorded essentially identical rainfall over periods of a week or more both before and during our expedition. The records from these two gauges were assumed to represent the atoll rainfall as a whole.

The following equations refer to mean ocean and lagoon salinity as S_O and S_L, respectively, and the mean daily rain volume as V_R. V_E is the exchange volume as defined in equation (3). Only water flowing in or out of the passes exchanges salt between the ocean and the lagoon; rainfall does not. Yet rain does contribute to total water input; for the lagoon volume to stay constant, outflow must equal the sum of ocean water inflow plus rain input (equation 2). The salt budget can be represented by the following three equations:

$$\text{Daily salt output} = V_E S_L \tag{5}$$

$$\text{Daily salt input} = (V_E - V_R)\, S_O \tag{6}$$

Since lagoon salinity is assumed to have reached a steady-state (constant) value, salt input equals salt output:

$$V_E S_L = (V_E - V_R)\, S_O \tag{7}$$

Combining equations (3) and (7) yields:

$$\tau = V_L V_R^{-1} (S_O - S_L)\, S_O^{-1} \tag{8}$$

The ratio of lagoon volume to daily rainfall volume is equivalent to the ratio of lagoon depth ($Z \approx 5$ m, according to Roy and Smith 1971) to daily rainfall height (h, in meters). Equation (8) can be modified accordingly:

$$\tau = Zh^{-1}(S_O - S_L)\, S_O^{-1} \tag{8a}$$

Most of our lagoon salinity measurements were made between 23 July and 1 August 1972. Mean rainfall from June through July was 1.5 cm/day (Taylor 1973, plus additional unpublished data gathered at the cable station). That value in equation (8a), 34.8‰ for S_O, and 31.5‰ for S_L (Table 1) give a mean residence time of 32 days. Thus, the two estimates of τ based on equations (4) and (8a) are each about 1 month, the value used in our subsequent calculations.

It is worth speculating briefly about the lack of a significant ocean-to-lagoon salinity differential during January 1970 (Gordon and Schiesser 1970). Data in Taylor (1973) show that rainfall during and immediately preceding the 1970 expedition was near normal, and data in Wyrtki (1966) and Taylor (1973) show that rainfall approximately equals evaporation during December and January. That situation should not generate an ocean-to-lagoon salinity differential. On the other hand, 1969 total rainfall was about 35 percent above normal; and mean rainfall ordinarily exceeds evaporation by about 1 meter in the vicinity of Fanning. Were the 340-day maximum residence time estimate of Gallagher et al. (1971) a close estimate of the true residence time, then the lagoon salinity would have been depressed to well below 30‰ in January 1970.

The assumptions of steady-state salinity, spatially constant rainfall, and low groundwater input apply to the lagoon as a whole and do not rigorously describe the age of individual water parcels. For example, the low salinity "rim" about the periphery of the lagoon (Fig. 2) surely represents an "edge" effect from groundwater seepage. Nevertheless, the salinity maps (particularly those in Fig. 4, crudely corrected according to the procedure described on p. 233 for groundwater effects) are likely to represent a general pattern of relative water age. That is, "pockets" of water, probably up to 2 months old, occur near the central portion of the north and south basins of the lagoon, while water near the passes has resided in the lagoon no more than a few tide cycles.

Responses of Lagoon Water Composition to Controlling Processes

A procedure of stepwise data analysis can be employed to estimate the contribution of various processes to the CO_2 content of lagoon waters. The first of these processes to be considered is gas exchange. Carbon dioxide partial pressure in lagoon waters (P_{CO_2}) can be calculated from *p*H and total alkalinity (appendix). During our survey, virtually the entire lagoon had surface-water P_{CO_2} values well

above the atmospheric mean of about 320 μatm. Values near the lagoon margin were below 400 μatm, while lagoon-center values were greater than that value.

Values were too variable to allow the P_{CO_2} to be contoured satisfactorily. This variability probably represents, in part, the relatively large errors inherent in calculating P_{CO_2} from water chemistry data (Keeling 1968). Nevertheless, our mean values are based on a sufficient number of data points to be reliable. Ocean water entering English Harbor averaged 370 μatm; for comparison, Keeling, Rakestraw, and Waterman (1965) reported central Pacific surface waters between 340 and 380 μatm. The mean lagoon surface water value was 400 μatm, so various processes apparently had raised the lagoon water P_{CO_2} by about 30 μatm, to about 80 μatm above the atmospheric value.

Any gas transfer between lagoon waters and the atmosphere should represent net evasion in order that lagoon P_{CO_2} values be lowered toward the atmospheric level. Both the experimental work of Sugiura, Ibert, and Hood (1963) and the theoretical calculations of Keeling (1965) suggest that an appropriate CO_2 evasion coefficient is probably something less than 0.018 moles m^{-2} $month^{-1}$ μatm^{-1}. With a mean air-to-sea differential of about 80 μatm, this maximum evasion coefficient yields a gas evasion rate of about 1.4 moles m^{-2} $month^{-1}$. There is no reason to believe that this process is subject to gross variation, although variations in wind speed and lagoon-water P_{CO_2} will affect the rate somewhat. Our estimate is probably an upper limit unless the lagoon water P_{CO_2} that we measured was particularly below usual values. A lower limit on gas evasion from the lagoon waters is zero; unless the air-to-sea P_{CO_2} gradient sometimes reverses direction, there should be no net CO_2 invasion. The oceanic water feeding the lagoon has a P_{CO_2} value about 50 μatm above the atmospheric value, and we consider it unlikely that processes in the lagoon ever alter the CO_2 content sufficiently to reverse the direction of the observed gradient. Limited data gathered in 1970 (Gordon and Schiesser 1970) and in 1973 (Dyrrsen 1973) also suggest lagoon P_{CO_2} values significantly above atmospheric.

Fig. 3, a plot of salinity versus total alkalinity, can be used to calculate the effects of freshwater dilution and calcification. The dense cluster of points at salinities higher than about 30‰ represents the bulk of the lagoon water. Point *A* represents mean ocean water. Salinities downward to near 0‰ come from the periphery of the lagoon, including the tidal inlets described by Guinther (1971 and this issue). Values at 0‰ include samples from water wells and other sites directly accessible to the freshwater lens of the atoll.

Rainwater dilution of ocean water, free of other influences, would alter the composition of that water along line *AB*, from pure ocean water (*A*) toward pure rainwater (*B*). Groundwater dilution alone would move ocean water along line *AD* if 3 meq/liter is an appropriate groundwater alkalinity (Table 1). If 5 meq/liter is a more appropriate groundwater alkalinity, then point *D* and line *AD* would be adjusted accordingly. $CaCO_3$ precipitation alone would lower total alkalinity with negligible effect on salinity (line *AA'C*). Water is altered by a combination of these processes, so the alteration pathways are more complex than have been described so far. The following assumption allows us to sort out these combined processes.

Line *A'E* of Fig. 3 has been drawn along an obvious boundary of data points above a salinity of 31‰. Below that salinity, the lower boundary of the points deviates markedly from the line. No samples have undergone a sufficient alkalinity change relative to salinity depression to fall significantly below that line. We interpret the line to represent the alteration path of samples subjected to the net effect of calcification and rainfall dilution without a significant contribution from groundwater dilution. Over most of the salinity range encompassed by lagoon water, line *A'E* is an acceptable representation of the boundary.

Most samples are subjected to groundwater dilution as well as to rainwater dilution and calcification. Such groundwater dilution moves samples from the position they would occupy somewhere along line *A'E* in the absence of groundwater, toward point *D*. Some hypothetical sample at point *F* would have had the composition found by projection from point *D* through point *F* to point *I* on line *A'E* in the absence of a groundwater component. Such a

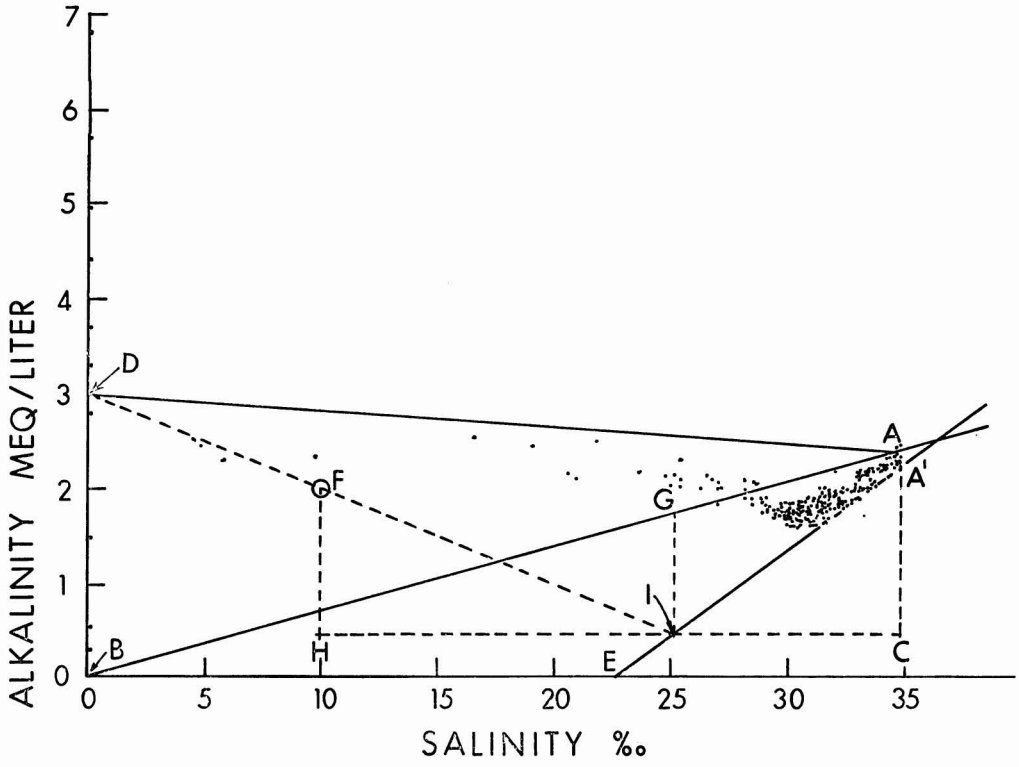

FIG. 3. Total alkalinity versus salinity at Fanning Island. The various letters and lines are explained in the text.

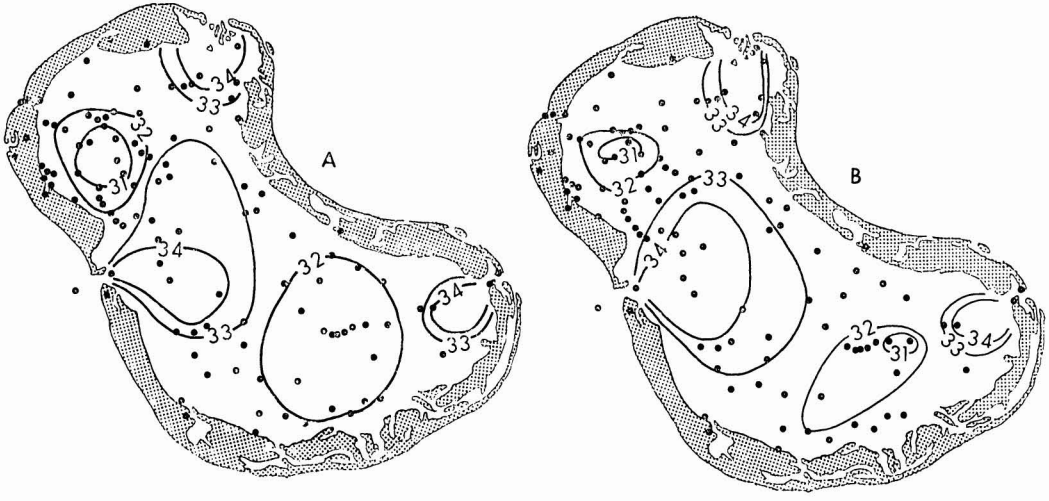

FIG. 4. Surface (A) and near-bottom (B) salinity maps from which the groundwater effect has been removed according to the procedure discussed in the text.

"groundwater-corrected" composition can be determined either graphically or algebraically for each sample point. From the geometry of the diagram and the location of most of the sample points, it can be seen that the groundwater-corrected composition for most points is not particularly sensitive to the alkalinity at point *D*.

For hypothetical sample point *F* projected back to line *A'E*, the distances *IC* and *IH* partition freshwater dilution (*CH*) between rainwater and groundwater. Moreover, the distance *IG* is the alkalinity depletion attributable to calcification. Equivalent constructions can be made for each sample point on the diagram.

Projecting points back to a groundwater-corrected salinity also allows the construction of salinity maps from which the groundwater component has been crudely removed (Fig. 4). Planimetry of the areas between contour lines on those maps yields a mean groundwater-corrected lagoon salinity of 32.7‰ if *D* is 3 meq/liter. This salinity, together with the mean ocean and lagoon salinities given in Table 1, suggest the mean ratio of ocean water: rainwater: groundwater in the lagoon to have been 91:6:3 during the summer of 1972. If *D* is 5 meq/liter, then the groundwater-corrected salinity averaged 32.1‰; and this ratio was 91:8:1 at the time of our survey.

The ratio of lagoon area to land area (about 5:1) suggests that most fresh water in the lagoon was probably derived directly from rainwater; hence, the second ratio and a mean groundwater alkalinity near 5 meq/liter are likely to be most nearly correct. However, either combination of freshwater dilution processes would have lowered the CO_2 content of the lagoon by closely comparable amounts. The values in Table 1 can be used to calculate the expected CO_2 content of a mixture of ocean water, rainwater, and groundwater in either of the above ratios:

$$\Sigma CO_2 = 0.91(2.0) + 0.06(0.0) + 0.03(3.0) = 1.91 \text{ moles/m}^3 \quad (9)$$

$$\Sigma CO_2 = 0.91(2.0) + 0.08(0.0) + 0.01(5.0) = 1.87 \text{ moles/m}^3 \quad (10)$$

This mixture has been estimated to result from water with a mean residence time of 1 month, so that freshwater dilution of ocean water to the mean lagoon salinity apparently lowers ΣCO_2 by about 0.1 moles m^{-3} $month^{-1}$ or, over the 5-meter mean lagoon depth, 0.5 moles m^{-2} $month^{-1}$. The effect of freshwater dilution is undoubtedly highly variable in response to variations in rainfall. For example, Gordon and Schiesser (1970) reported no difference between ocean and lagoon salinity during January 1970, suggesting no net freshwater component to the CO_2 budget at that time. Samples gathered in March 1973 by Dyrrsen (1973) suggest some salinity depression in the lagoon, but these data are insufficient to estimate the amount of depression. Rainfall records since 1907 (Taylor 1973) reveal few sustained periods with greater rainfall than we observed, so that the CO_2 depression we observed in response to freshwater dilution was larger than usual.

The divergence of lines *AB* and *A'E* (Fig. 3) from one another can be used to estimate the calcification rate in the lagoon. Line *AB*, which demarks the pathway which would be taken by seawater only altered by dilution with rainwater, has a slope of about 0.07 meq $liter^{-1}$ $‰^{-1}$. Line *A'E*, interpreted to represent the net effect of calcification and rainfall dilution in the absence of groundwater dilution, slopes about 0.20 meq $liter^{-1}$ $‰^{-1}$. The difference between the slopes of these two lines—that is, the slope attributable to calcification alone—is 0.13 meq $liter^{-1}$ $‰^{-1}$.

The previous discussion has suggested that rainfall lowered salinity of water in the lagoon by about 2.7‰ $month^{-1}$. Multiplying this dilution rate by the calcification-induced alkalinity/salinity slope yields a rate estimate: 0.35 meq $liter^{-1}$ $month^{-1}$. ΣCO_2 is lowered by 0.5 moles for each equivalent of total alkalinity depression during calcification, so calcification lowered the ΣCO_2 by 0.175 moles m^{-3} $month^{-1}$ (or about 0.9 moles m^{-2} $month^{-1}$ through the 5-meter water column).

Some evidence for consistent deviations from this mean rate can be inferred from Fig. 3. The offset of point *A'* from point *A* may represent initial rapid calcification from ocean water before the salinity of that water was significantly lowered by dilution. Dyrrsen (1973) estimated the calcification rate suggested by a single water sample, which he gathered in

TABLE 2

CARBON DIOXIDE BUDGET FOR FANNING LAGOON

PROCESS	MEAN MONTHLY CHANGE moles/m³	moles/m²	COMMENTS
Gas Evasion	0.00 to −0.28	0.0 to −1.4	Based on minimum to maximum gas evasion rate constants
Freshwater Dilution	−0.10	−0.5	From equations (9) and (10)
Calcification	−0.18	−0.9	Difference in slopes between lines AB and A'E of Fig. 3
Organic Carbon Production (−) or Consumption (+)	−0.02 to +0.26	−0.1 to +1.3	Difference between net CO_2 change (below) and the sum of the terms given above
Net	−0.30	−1.5	Sum of the above terms. Also follows from Table 1.

NOTE: The calculations are based on an estimated mean lagoon water residence time of 1 month and a mean lagoon depth of 5 meters.

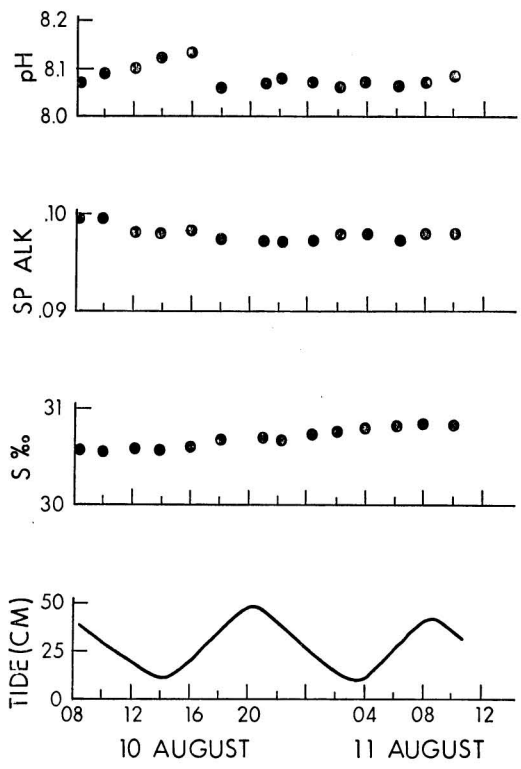

FIG. 5. Variation of tide height, salinity, specific alkalinity, and *p*H over a 1-day cycle at Suez Pond.

March 1973 1,000 meters southeast of English Harbor, to be 0.0063 moles m^{-3} $hour^{-1}$. It is difficult to relate quantitatively an estimate based on a single sample with our more extensive data, but this value is qualitatively consistent with rapid alkalinity depletion of water immediately upon its entrance into the lagoon. At low salinities, the deviation of points from line *A'E* may result from eventual decrease in calcification rate with no increase in dilution rate. Over the majority of the salinity range encountered in the lagoon, the straight-line approximation fits the data well. Further attention will be given in the discussion to the possible significance of such variations in the calcification rate.

Organic carbon production can be estimated as the difference between the total rate of CO_2 changes in the lagoon and the sum of those terms previously estimated. Table 2 summarizes those terms. Within the uncertainty limits attached to the estimate of gas exchange, net organic carbon production in the lagoon did not differ significantly from zero during our survey. The possible range of organic carbon flux consistent with our data is −0.1 moles m^{-2} $month^{-1}$ (net production) to +1.3 moles m^{-2} $month^{-1}$ (net consumption). Interpretation of these results will be deferred to the discussion.

Temporal Variation in Lagoon Composition

Schmalz and Swanson (1969) criticized earlier analyses of CO_2 data from reef systems because those analyses ignored diurnal cycles in

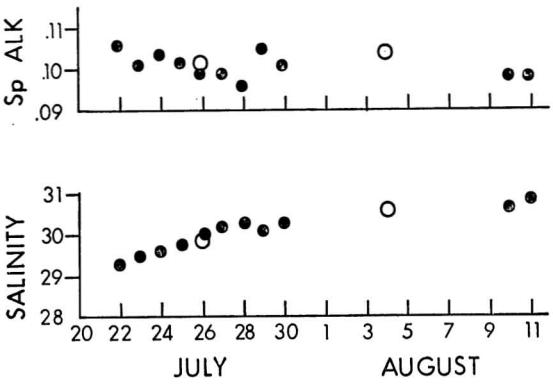

FIG. 6. Mean salinity and specific alkalinity at Suez Pond from 22 July to 11 August 1972. Open circles represent sampling stations other than the standard, repeated station.

the concentration and partitioning of CO_2 in seawater. To minimize this source of potential variability, we gathered most samples for our lagoonwide sampling survey between middle and late morning. We also conducted a daylong sampling series at Suez Pond (Fig. 1) to determine the likely magnitude of diurnal cyclicity to the Fanning Lagoon CO_2 system. That location was chosen to be out of direct influence from both ocean water exchange and groundwater seepage but sufficiently close to our laboratory to be reached by skiff at night.

Salinity effects on total alkalinity have been "normalized" out of these diurnal cycle data by the calculation of specific alkalinity (total alkalinity/chlorinity). Actually, the salinity effect is small, because salinity varied by only about 0.6‰ at a given depth during the 1-day sampling period.

Fig. 5 qualitatively confirms the *p*H trends observed by Schmalz and Swanson (1969) but shows no strong trend in specific alkalinity. Diurnally varying *p*H and a constant total alkalinity will yield a diurnal variation in carbonate alkalinity and other CO_2 parameters. Nonetheless, the diurnal variation in CO_2 parameter was only a small fraction of the geographic variation encountered during this study. Thus, while we concur with the general expectation of a diurnal CO_2 cycle discussed by Schmalz and Swanson, we do not find such a cycle to be quantitatively significant in the lagoon. Diurnal periodicity there superimposes only a small oscillation upon the much greater effects of a month-long history of water "incubation."

Certainly there is longer term variation in the composition of lagoon waters. In particular, we evaluated our assumption that the lagoon salinity had reached a steady-state composition by the time of our sampling.

Water samples were gathered in Suez Pond about noon on most days of our survey. Additional data are available for each of the days spanned by our 1-day survey (10 to 11 August) and for 4 August. Fig. 6 shows evidence of an increase in mean salinity from about 29.3‰ to about 30.6‰ over several days.

Increasing salinity is not obviously consistent with a gradual adjustment of the lagoon salinity to the heavy rainfall regime which prevailed during our stay. Nor is such a changing salinity indicative of an entirely steady-state system. We suggest that superimposed on a generally steady-state pattern there may have been minor oscillations of lagoon salinity in response to lunar cycles in the tide range and flushing characteristics of the lagoon. Moreover, the general agreement between one residence time calculation dependent on the assumption of steady-state salinity and a second calculation independent of that assumption (pp. 229 to 230) suggests that any departure of lagoon composition from steady state was relatively small.

A final aspect of temporal variability comes from comparing our data from Suez Pond with other available data. We found the average salinity of that pond to be 30‰, while four values in January 1970 (Gordon, Fournier, and Krasnick 1971) averaged 35‰. A drought which began in April 1973 was sufficient to raise the salinity of Suez Pond to 37‰ by November 1973 (two samples collected by M. Vitousek and R. Taylor).

Specific alkalinity values reported by Gordon, Fournier, and Krasnick (1971) for Suez Pond averaged 0.109, compared with 0.101 for our 1972 data. Considering slight differences in analytical technique between the two studies, as well as the range of alkalinity values which we found in Suez Pond (Fig. 6), we doubt that this difference in specific alkalinity is significant.

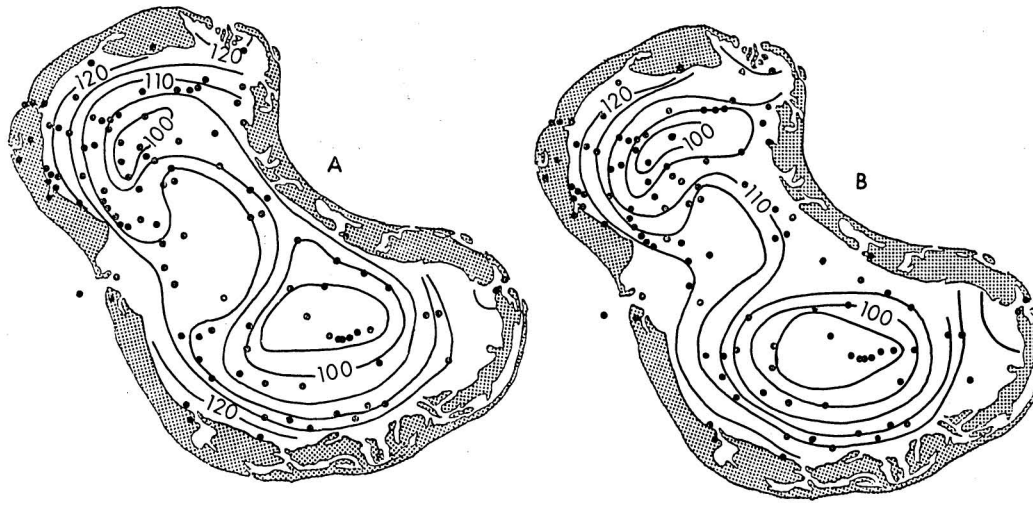

FIG. 7. Surface (*A*) and near-bottom (*B*) maps of (specific alkalinity $\times 1000$) in Fanning Lagoon.

Both our values and the earlier ones are distinctly different from constant offshore values of 0.122. The various data cited above suggest that the temporal variability in specific alkalinity is considerably less than the temporal salinity variations in the lagoon.

Vertical and Horizontal Variations in Lagoon Composition

Maps of both salinity and specific alkalinity (Figs. 2 and 7) show considerable variation in the lagoon composition. Characteristically, values near the passes are similar in composition to oceanic values. This pattern reflects the relatively recent oceanic derivation of such water. Near the land, lagoon water has high specific alkalinity and low salinity due to the contribution of groundwater. The low salinity rim is absent when the water composition is corrected for the groundwater contribution (Fig. 4). Water in both the north and the south basins, away from the lagoon margins, has low alkalinity and intermediate salinity due to the small groundwater contribution, large rainfall component, and relatively long history of calcification. Samples of this water tend to fall near line *A'E* of Fig. 3.

Vertical variations in lagoon composition are considerably less prominent than the horizontal gradients. Generally there is a slight increase in salinity with depth. Only in the vicinity of the passes does this increase express itself as well-defined stratification. There the tidal influence of incoming high-salinity ocean water to a great extent offsets the effective vertical mixing which prevails through much of the lagoon (Stroup and Meyers, this issue).

Percent $CaCO_3$ Saturation of Lagoon Waters

Percent $CaCO_3$ saturation is commonly defined (e.g., by Berner 1971) to be 100 times the ratio of seawater $CaCO_3$ ion activity product (*IAP*) to the solubility product constant (K_{sp}) of the mineral of interest. Discrepancies between investigators in estimating the saturation state of seawater can be attributed to different estimates of the calcium and carbonate activity coefficients (γCa and γCO_3) and of the appropriate K_{sp}. Following Berner (1971), we have used 0.20 and 0.02 for γCa and γCO_3, respectively. Fig. 9 summarizes the K_{sp} values we have used. Details of our calculations are reported in the appendix.

Using these values, we have found that oceanic water is approximately 200 percent saturated with respect to the K_{sp} of aragonite (Fig. 9). This value is in substantial agreement with Lyakhin (1968) whose map shows ocean surface waters near Fanning to be approximately 300 percent saturated with respect to aragonite.

By contrast, lagoon waters show greatly

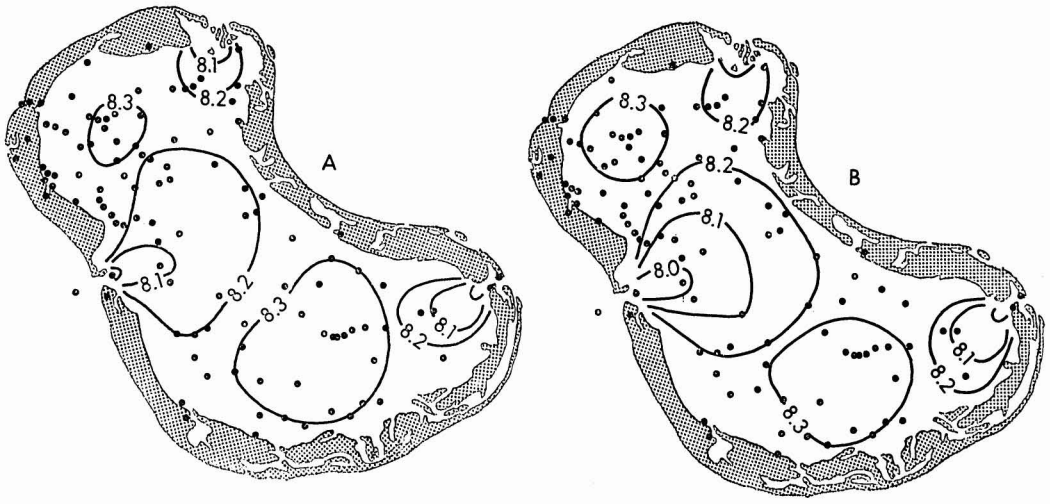

FIG. 8. Surface (*A*) and near-bottom (*B*) maps of (− log *IAP*) in Fanning Lagoon.

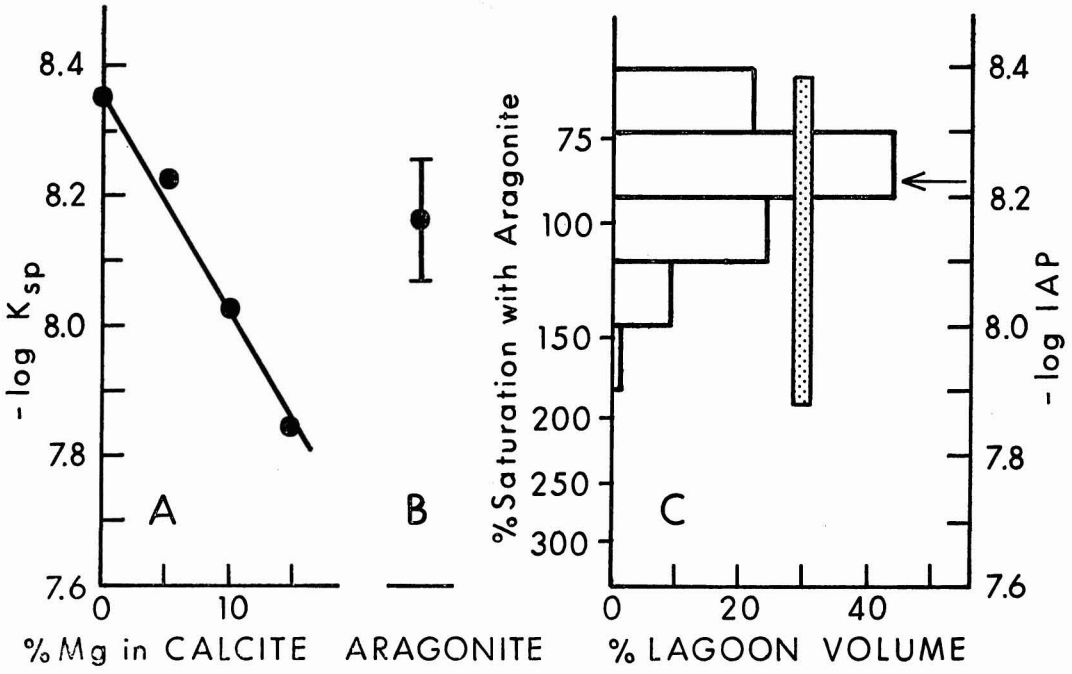

FIG. 9. Diagram comparing (− log k_{sp}) of various Mg-calcites (*A*, from data in Winland 1969) and aragonite (*B*, from Winland 1969, Smith 1941, Cloud 1962, and from a summary of values in Broecker and Takahashi 1966) with the frequency distribution of (− log *IAP*) in Fanning Lagoon (*C*). The arrow and vertical bar on part *C* represent the lagoon mean and the range of *IAP* values encountered in the lagoon and adjacent ocean waters, respectively.

depressed *IAP* values. Fig. 8 shows maps of *IAP* values, and Fig. 9*c* is a histogram of *IAP* as a function of percent lagoon volume. There is a slight discrepancy between our calculated values and measured saturation states; three samples calculated to be 95 to 100 percent saturated with respect to calcite tested (by the saturometry technique of Weyl 1961) to be slightly supersaturated with respect to reagent-grade $CaCO_3$ (calcite).

Even with allowances for some uncertainty in absolute saturation states, it is evident that lagoon waters are approximately saturated with respect to aragonite and that the average lagoon saturation state is less than half that of the adjacent open ocean water. This depressed saturation state is similar to that observed by Broecker and Takakashi (1966) across the Bahama Banks and can be ascribed to the interacting biological, chemical, and physical processes which have so drastically altered to CO_2 composition of lagoon water.

DISCUSSION

Our budget has demonstrated the significance of various pathways of CO_2 flux in the lagoon of a coral atoll. Of particular interest are the metabolically important processes of organic carbon production and calcification.

Data for the windward reef flat of Eniwetok Atoll (Smith 1973, Smith and Marsh 1973) suggest that instantaneous rates of CO_2 flux associated with organic carbon production exceed the instantaneous flux associated with calcification there. Water remains on the reef flat of Eniwetok only a few minutes, so any impact of CO_2 changes in the water on that system must be in response to such instantaneous flux patterns.

By contrast, water in Fanning Lagoon undergoes a month-long history of CO_2 alteration; the reef system is exposed to the results of the integrated, rather than of the instantaneous, record of these processes. The absolute effect of organic carbon production on the CO_2 system in that lagoon is certainly not much larger than the calcification effect and is probably smaller (Table 2).

Corals knolls and reefs cover over 40 percent of the lagoon floor at Fanning, and live corals themselves occupy over 30 percent of the lagoon area (Roy and Smith 1971). While we recognize that the corals themselves are probably not the major metabolic component of reefs (discussed, e.g., by Smith and Marsh 1973), we suggest that their presence is probably a reliable indicator of the high metabolic activity which most investigators attribute to coral reef communities. For example, previously described reef flat communities (summarized in Helfrich and Townsley 1963; Stoddart 1969; Smith and Marsh 1973) have gross production rates exceeding 3 g C m^{-2} day^{-1}. The organic carbon flux of the community in Fanning Lagoon, inclusive of benthos, nekton, and plankton, lies between a net production rate of 0.04 g C m^{-2} day^{-1} and a net consumption rate of 0.5 g C m^{-2} day^{-1} (as calculated from Table 2). Thus, even if Fanning Lagoon has the high daytime metabolic activity which characterizes other reef communities, it has no significant net carbon production. Any daytime excesses are apparently consumed at night. In fact, the data suggest that some net carbon input may be necessary to support the lagoon reef ecosystem.

Gordon, Fournier, and Krasnick (1971) reported on the ^{14}C productivity of Fanning Lagoon and suggested that plankton productivity there is high compared with that of other lagoons. Unfortunately, more recent and more extensive ^{14}C measurements by Krasnick (1973) suggest that ^{14}C measurements by conventional techniques in the turbid waters of that lagoon are probably unreliable, largely because of ^{14}C exchange between the suspended $CaCO_3$ particles and the incubation medium. However, even if the net productivity of the Fanning Lagoon is as low as that of other lagoons listed by Gordon, Fournier, and Krasnick (0.025 to 0.1 g C m^{-2} day^{-1} through the 5-meter water column), then the lagoon reef benthos plus nekton are almost certainly slight net heterotrophs.

Our survey was conducted during a period of generally heavy cloud cover. We suggest that this consideration might shift the carbon flux to be expected under more usual conditions of greater light intensity slightly back in the direction of net carbon production, but any such shift seems likely to be small. Thus, our

estimate representing a record of carbon flux integrated over a time span of a month and an area of 100 km^2 is indistinguishable from zero.

Two additional observations further support the likelihood that net organic carbon production is near zero. Schiesser (in Gordon 1971) found that Fanning sediments only have about 0.1 percent organic carbon, a Figure in general agreement with the low organic carbon content reported for the sediment of other coral atolls (Emery, Tracey, and Ladd 1954). Moreover, Gordon (1971) suggested that suspended plus dissolved organic carbon flux to and from Fanning Lagoon via the passes amount to only about 0.01 moles C m^{-2} month^{-1}, a negligible fraction of the CO_2 budget (Table 2). Thus, the lagoon does not appear to be a significant source or a sink for organic carbon. It seems likely therefore that the community of Fanning Lagoon, and perhaps the communities of other atoll lagoons as well, produce almost exactly as much organic carbon as they consume.

By contrast, $CaCO_3$ precipitation does result in net carbon flux. The data of Smith et al. (1971) suggest that there is little or no net transport of this $CaCO_3$ from the lagoon, although there is apparently some exchange of $CaCO_3$ precipitated in the lagoon for $CaCO_3$ originating on the ocean reef outside the lagoon.

Biological calcification accounts for most or all of the $CaCO_3$ precipitation in the lagoon. Scanning electron microscopy of lagoon muds reveals the grain to be predominantly blocky fragments, including composite grains of lath-like bundles resembling the pelecypod and coral debris illustrated by Hay, Wise, and Stieglitz (1970). Much of the material has a maximum diameter of less than 5 microns, a size that precludes unequivocal resolution of phyletic origins. However, abundant corals living in the lagoon are probably the major $CaCO_3$ producers. The coral skeletons are broken down, probably in large part by the boring sponges that are found on the line reefs throughout the lagoon and also by boring bivalves. Some silt-sized grains in the mud look much like the chips of material resulting from sponge-boring (Cobb 1969, Rützler and Rieger 1973). This observation has been confirmed recently by Fütterer (1974). The observations by Neumann (1966), Cobb (1969), and Rützler and Rieger (1973) suggest that boring sponges dissolve less than 10 percent of the material that they erode, so such bioerosion should not lower net calcification estimated from alkalinity depletion significantly below gross calcification.

Our data (Table 2) indicate a net calcification rate of about 1 kg $CaCO_3$ m^{-2} yr^{-1}. Based on the abundance of live corals in the lagoon (> 30 percent cover, according to Roy and Smith 1971) and the known $CaCO_3$ production rates of common reef corals (> 10 kg $CaCO_3$ m^{-2} yr^{-1} per square meter of cover, according to Chave, Smith, and Roy 1972), we would have expected the $CaCO_3$ production rate to have been at least three times as high as the observed rate. That estimate, while subject to considerable uncertainty, is likely to err by being too low; it is based on the lower estimates of coral cover and production rate, and the estimate does not include $CaCO_3$ production by organisms other than corals in the lagoon. The large discrepancy between estimates of $CaCO_3$ production based on water chemistry and on expectations based on coral standing crop-growth data, and the observation that the $CaCO_3$ ion activity product of water in Fanning Lagoon is near the solubility product constant of aragonite (Figs. 8 and 9) provide a basis for speculating about factors which might affect the calcification rate of marine organisms.

Two alternative explanations could link these observations. Total gross calcification may proceed at a rate well in excess of 1 kg $CaCO_3$ m^{-2} yr^{-1}, but re-solution of $CaCO_3$ may increase the alkalinity and offset much of this gross calcification. The resultant net calcification rate would represent the balance between $CaCO_3$ precipitation and solution but would be largely attributable to solution. Such a model ascribes the low net calcification rate and the $CaCO_3$ ion activity product of lagoon waters to relatively rapid and thermodynamically controlled solution, in accord with the view of Schmalz (1967) and Schmalz and Swanson (1969) that seawater is usually in thermodynamic equilibrium with the most soluble $CaCO_3$ mineral with which that water is in contact.

There appear to be several problems with such an interpretation. Most of the lagoon water is approximately saturated with respect to

aragonite; some of the water is apparently even saturated with respect to low-Mg calcite, which is far less soluble than aragonite (Figs. 8 and 9) Yet in addition to abundant aragonite, 15 mole-percent Mg calcite (roughly twice as soluble as aragonite, according to Fig. 8) is present both in the sediments and among the suspended materials (Smith et al. 1971; Smith and Roy, unpublished X-ray diffraction data). Moreover, scanning electron microscopy of the lagoon muds provides no evidence for grain etching, which should accompany extensive solution of calcareous materials.

An alternative mechanism to explain this situation seems more plausible. The $CaCO_3$ ion activity product of seawater or something closely related to that product may limit the calcification of some marine organisms. Certain calcifying organisms (such as corals) may be able to calcify only when the aqueous medium surrounding them exceeds some minimum $CaCO_3$ ion activity product. The effect of *IAP* may be similar to that of other limiting constituents; that is, organisms may slow their calcification rate as the surrounding medium approaches some limiting *IAP*.

Such a model does not take issue with the various models (e.g., Goreau 1959, Simkiss 1964, Pearse and Muscatine 1971) that have been advanced to explain coral calcification; rather, we suggest that some process may affect the supply of ions from seawater to the calcification sites of corals and some other calcifiers before any of the internal controls can exert themselves. Recent experiments (Smith, unpublished) demonstrate that direct manipulations of the CO_2 system in aquaria by additions of acid or base can alter the calcification rate of corals in those aquaria. Recognized correspondence between photosynthetic activity and calcification rate (Goreau 1959, Pearse and Muscatine 1971) can also be attributed to alterations of the CO_2 system external to the organism, rather than to (or in addition to) the internal effects postulated by those authors.

If such a model of external *IAP* control of biological calcification is at least partially correct, then the effect of Ca^{++} on the calcification rate of marine organisms would tend to be less than the CO_3^{--} effect. The concentration of Ca^{++} is large and essentially invariant in ocean water, while CO_3^{--} is present in low and variable quantities. Hence, the latter ion is the more important ion to the product of the two.

The proposed model is by no means universal. For example, Chave (personal communication) has observed abundant barnacles living along the shore of the Gulf of Alaska in waters undersaturated with respect to the low-Mg calcite which those organisms precipitate. We suspect that many mollusks and echinoderms may exhibit similar hardy ability to calcify in low-*IAP* waters. However, sediments rich in reef components such as hermatypic corals and calcareous green algae are much more restricted in latitudinal distribution (Hayes 1967, Lees and Buller 1972) and are not described from waters undersaturated with respect to their mineral phase (aragonite).

Rodgers (1957) and others have suggested that a general restriction of calcareous sediments to the tropics might be largely attributable to the presence there of waters highly supersaturated with respect to $CaCO_3$. Chave (1967) pointed out two misconceptions associated with that statement. In the first place, virtually all surface open ocean water, even that at high latitudes, is supersaturated with respect to calcite. Secondly, as has already been mentioned, calcareous sediments are produced at high latitudes. Yet, despite erroneous bases for associating $CaCO_3$ deposition with supersaturation, our data suggest that the saturation-state mechanism for limiting $CaCO_3$ production may work in some situations.

Broecker and Takahashi (1966) used the proportional relationship between $CaCO_3$ precipitation rate and the degree of $CaCO_3$ supersaturation on the Bahama Banks as an argument that precipitation of aragonite muds there was probably largely inorganic. However, such proportional relationships generally describe the response of metabolism to any limiting factor. Moreover, Neumann and Land (1969) and Stockman, Ginsburg, and Shinn (1967) have offered convincing evidence that biological processes probably account for most or all of the aragonite mud precipitation on the Bahama Banks and other similar environments. The $CaCO_3$ muds in Fanning Lagoon are obviously biogenic (p. 239), and our data hint of a change in calcification rate similar to that documented

by Broecker and Takahashi (1966). In both areas cited as possible examples of an *IAP* limitation to biological calcification (Fanning and the Bahamas), aragonite is the overwhelming mineral phase precipitated—as is generally true for areas of tropical neritic carbonate sedimentation. The high latitude sediments described as exceptions to such a model are dominantly calcite. Hence, the suggestion that *IAP* might limit the $CaCO_3$ production rate of marine ecosystems so far finds support only in calcifying systems dominated by aragonite precipitation.

Several other possible limitations to calcification also merit attention. Temperature has been suggested as a possible control of coral calcification. However, the 29° C mean water temperature in the Fanning Lagoon during our survey lies near the optimum temperature for coral growth in Hawaii and Eniwetok (Clausen 1971, 1972; Coles 1973). Hence, temperature can be dismissed from further consideration as a likely factor suppressing calcification in the Fanning Lagoon during our survey.

Salinity was depressed during the 1972 expedition to below the 34 to 36‰ range which Wells (1957) considers to be optimum for coral growth. That optimum range is open to some question, however. For example, Yamazato (1970) found the calcification rate of a common Hawaiian coral to be relatively unaffected by salinities as low as 27‰. Moreover, the limited earlier data for Fanning Lagoon do not suggest that higher salinities are accompanied by lower specific alkalinity (Gordon, Fournier, and Krasnick 1971).

Light and/or turbidity is a complex factor or set of factors that might limit lagoon calcification. Much of Fanning Lagoon is very turbid because large concentrations of $CaCO_3$ are suspended in the water column (Smith et al. 1971; Stroup and Meyers, this issue). Roy and Smith (1971) pointed out that neither light attenuation nor sedimentation prevents survival of common reef biota in the lagoon. However, neither those authors nor we have sufficient information to evaluate the possible sublethal effects of turbid water on the energetics of the reef biota. If some aspect of water clarity does limit the calcification rate in Fanning Lagoon, then that influence is likely to be continuous; lagoon water there apparently remains turbid most of the time.

In fact, there is a possible relationship between the $CaCO_3$ ion activity product and the turbidity. Increased turbidity could, by lowering available light, also lower photosynthesis—hence *p*H, CO_3^{--} concentration, and the $CaCO_3$ ion activity product of the water.

CONCLUSIONS

Emery (1962), Schmalz and Swanson (1969), Kinsey (1972), and Smith (1973) have reported on coral reef systems showing marked diurnal oscillation in the CO_2 composition of their waters; the present study and that of Broecke and Takahashi (1966) describe reef systems which alter CO_2 biogeochemistry in a long-term, integrated fashion.

The high organic carbon metabolic activity of reef communities may, in many instances, result in diurnally imposed oscillations in the CO_2 content of associated waters. However, because coral reef communities apparently produce about as much organic carbon as they consume, such metabolic activity seems unlikely to impose long-term changes on the CO_2 content of those waters. That role on coral reefs is apparently reserved for $CaCO_3$ reactions, plus the physical processes of gas exchange, mixing of ocean water with fresh water, and evaporation.

While coral reefs are bathed by waters which are initially far supersaturated with respect to common $CaCO_3$ minerals (see, e.g., Lyakhin 1968), the combined physical configuration and biogeochemical characteristics of reef systems may make these systems unique in their ability to alter the CO_2 composition of the water impinging upon them. If that observation is correct, then coral reef communities are perhaps the most likely of all present-day marine communities to be affected by the availability and speciation of CO_2.

ACKNOWLEDGMENTS

We thank all of the other members of the Fanning II Expedition for their considerable physical assistance (particularly during the

Suez Pond survey) and for their criticisms of various drafts of this manuscript. In addition, the following individuals also provided helpful criticisms of the manuscript: Raymond Fosberg, Ian Macintyre, Jack Pierce, Robert Johannes, William Wiebe, Robert Buddemeier, David Hurd, Peter Kroopnick, Robert Garrels, and John Bardach. The Smithsonian Institution permitted the participation of S. V. Smith in this expedition and provided him both with travel funds and access to their scanning electron microscope, on the use of which he was ably guided by Walter Brown. Dennis Kam was instrumental in keypunching and debugging both the computer program and the data used for this study. Both Ronald Taylor and Martin Vitousek generously supplied information and samples. Finally, we thank Alison Kay and Keith Chave for inviting our participation in the expedition.

APPENDIX

The calculations summarized below, as well as an algebraic solution of the procedure outlined on p. 231 for the interpretation of Fig. 3, were carried out on the University of Hawaii IBM 360 computer.

The procedure for analyzing CO_2 data combines theoretical and empirical relationships either given in or derived from Park (1969), Skirrow (1965), or Berner (1971). First is needed a brief glossary of the symbols used in this appendix:

a_H, a_{OH}	Activity of hydrogen and hydroxide: 10^{-pH} and 10^{-pOH}, respectively; assumed equivalent to concentrations, in moles/liter.
B.A.	Borate alkalinity, in eq/liter: $(H_2BO_3)^- + 2(HBO_3)^{--}$.
C.A.	Carbonate alkalinity, in eq/liter: $(HCO_3)^- + 2(CO_3)^{--}$.
(Ca), (CO_3), etc.	Concentration of Ca^{++}, CO_3^{--}, etc., in moles/liter.
Cl	Chlorinity, in g/kg.
IAP	(Ca) (CO_3) ion activity product.
K'_{1c}, K'_{2c}, K'_{1b}, K'_{2b}	First and second apparent dissociation constants for carbonic acid and boric acid in seawater.
P_{CO_2}	Partial pressure of CO_2 in seawater, in atm.
S	Salinity, in g/kg.
t	Temperature, in °C.
T.A.	Total alkalinity, in eq/liter: $(HCO_3)^- + 2(CO_3)^{--} + (H_2BO_3)^- + 2(HBO_3) + (OH)^- - (H)^+$.
ΣB, ΣCO_2	Concentrations of the sum of carbonic acid and boric acid species in seawater, in moles/liter.
α	Henry's Law coefficient for CO_2 in seawater.
γCa, γCO_3	Activity coefficients for Ca^{++} and CO_3.

The CO_2-related parameters calculated for this investigation include ΣCO_2, P_{CO_2}, and *IAP*. The first of these is calculated for the water sample at laboratory temperature (25° C), while the other two are calculated at the appropriate field temperature (27° to 30° C). Let us consider each in turn. The direct sample measurements on which these calculations are made include temperature, total alkalinity, *p*H, and salinity.

ΣCO_2 is calculable from *C.A.*, a_H, and the dissociation constants for carbonic acid. *C.A.* is calculated from *T.A.* and *B.A.*, which, in turn, is a function of a_H, *Cl*, and the boric acid dissociation constants:

$$Cl = (S - 0.03)/1.805 \tag{a1}$$

$$\Sigma B = 2.06 \times 10^{-5}\, Cl \tag{a2}$$

$$B.A. = \Sigma B\,(a_H K'_{1b} + 2K'_{1b}K'_{2b})\,(a_H^2 + a_H K'_{1b} + K'_{1b}K'_{2b})^{-1} \tag{a3}$$

$$a_{OH} = 10^{-14}/a_H \tag{a4}$$

$$C.A. = T.A. - B.A. - a_{OH} + a_H \tag{a5}$$

$$\Sigma CO_2 = C.A.\,(K'_{1c}a_H + K'_{1c}K'_{2c} + a_H^2)(K'_{1c}a_H + 2K'_{1c}K'_{2c})^{-1} \tag{a6}$$

P_{CO_2} can be calculated from a_H, *C.A.*, and α:

$$P_{CO_2} = C.A.\; a_H^2\,[K'_{1c}\,\alpha\,(a_H + 2K'_{2c})]^{-1} \tag{a7}$$

Both the Henry's Law coefficient for CO_2 and the apparent dissociation constants for carbonic and boric acids are temperature and chlorinity-dependent. Over the temperature and chlorinity range encountered throughout most of Fanning Lagoon, the following linear approximations to Lyman's data (as given in the appendix of Riley and Skirrow 1965) are satisfactory:

$$K'_{1c} = 10^{-6}\,[0.55 + 0.024\,Cl] \tag{a8}$$

$$K'_{2c} = 10^{-10}\,[0.52 + 0.4\,Cl + 0.014t] \tag{a9}$$

$$K'_{1b} = 10^{-9}\,[0.5 + 0.08\,Cl] \tag{a10}$$

$$K'_{2b} = 10^{-11}\,[-0.3 + 0.69\,Cl] \quad \text{(a11)}$$

$$\alpha = 0.051 - 0.0002\,Cl^{-} - 0.0007t \quad \text{(a12)}$$

For freshwater samples, the appropriate constants were taken directly from the values reported in Riley and Skirrow rather than being derived from such empirical calculations.

IAP can be calculated from Berner's (1971) estimates of γ_{Ca} and γ_{CO_3} at the ionic strength of seawater (0.2 and 0.02, respectively), the relation of (Ca) to *Cl*, and the calculation of (CO_3):

$$(Ca) = Cl/1900 \quad \text{(a13)}$$

$$(CO_3) = C.A.\,K'_{2c}\,(a_H + 2K'_{2c})^{-1} \quad \text{(a14)}$$

$$IAP = \gamma_{Ca}(Ca)\,\gamma_{CO_3}(CO_3) \quad \text{(a15)}$$

The constant relationship between (Ca) and *Cl* (equation a13) does not strictly apply when some process other than evaporation or dilution by ion-free water alters the composition of seawater. The calculation of (Ca) according to that equation is subject to two small errors which tend to offset one another at Fanning. Text equations (9) and (10) have demonstrated that groundwater contributes an average of less than 0.1 mmoles/liter ΣCO_2—and probably (Ca)—to the lagoon water. According to the discussion on p. 233, calcification has lowered ΣCO_2, and also (Ca), by about 0.2 mmoles/liter. These two effects suggest a net overestimate of (Ca) by equation (a13) of less than 0.2 mmoles/liter, or less than about 2 percent.

The above situation causes a small error in calculating *IAP*, but a far more serious potential error comes from the estimates of γ_{Ca} and γ_{CO_3}. The activity coefficient product which we have used is 0.0040, while the product of the γ_{CO_3} and γ_{Ca} coefficients reported by Garrels and Thompson (1962) is 0.0048. The resultant discrepancy between *IAP* value derived from each of these two products is 20 percent. Such a discrepancy makes it particularly difficult to compare results between investigators but should not affect the internal consistency within any given study.

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